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EQUILIBRIUM IN THE SYSTEMS SILVER BROMIDE AND PYRIDINE AND SILVER IODIDE AND PYRIDINE

BY

ERNEST CHRISTIAN McKELVY

A Thesis Submitted for the Degree of
MASTER OF ARTS

UNIVERSITY OF WISCONSIN
1908

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Kahlenberg and Wittich (1) have recently investigated the two component system silver chloride and pyridine. Up to that time there had been no systematic investigation of the silver halide addition products of pyridine and the conditions necessary for their existence. The work with these salts and pyridine has been confined to the isolation, description and analyses of the compounds separating out under arbitrarily chosen and none too well defined conditions.

Varet (2) describes the compounds pyridine silver bromide($AgBr.C_5H_5N$) and pyridine silver iodide($AgI.C_5H_5N$). He was unable to obtain an addition product with silver chloride because none are stable above 0°.(conf. ref.(1)). Stanislaus von Laszczynski (3) mentions the compound pyridine silver iodide. Work with the other organic bases of the pyridine group has been of the same character. Werner and Ferschland (4) prepared and described silver halide addition products of piperidine. Tombeck (5) determined the dissociation curve for picoline silver iodide($2AgI3C_5H_5N$), and also prepared the silver halides with varying amounts of picoline, lutidine and collidine of crystallisation.

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(1).Thesis-Univ. of Wis. (1908).
(2).Bull. (3) 5, 847. (1891).
(3).Dissertation-Univ. of Berlin. (1894.)
(4).Zeit. anorg. Chem. 15,8. (1897).
(5).An. Chim. phys. (7) 21, 467.(1900).

Renz (6) and Wuth (7) have prepared silver halide addition compounds with salts of pyridine and the pyridine bases, as silver chloride pyridine chlorhydrate($AgCl.C_5H_5N .HCl$).

Among the other salts of silver in combination with pyridine Varet (l.c.) mentions pyridine silver cyanide ($AgCN.C_5H_5N$). Klobb (8) describes the compound pyridine silver permanganate($AgMnO_4.5C_5H_5N$). Kahlenberg and Brewer (9) have worked out completely the equilibrium conditions in the system silver nitrate- pyridine and interpreted them according to the phase rule. The literature contains no mention of any compounds of this base with silver fluoride.

It was thought desirable to investigate and establish the equilibrium curves in the systems silver bromide-pyridine and silver iodide-pyridine. For that purpose the following work was undertaken. It consists in determining by experiment the composition of the phase, saturated solution, present at various temperatures and the nature of the solid in contact with it. At this time the investigations were not carried below -20°. During the hot weather it was found impossible to keep the temperature constant for a long enough time to permit the system to come to equilibrium.

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(6).Ber. 35, 1954 (1902).
(7).Ber. 35, 2415 (1902).
(8).Bull. (3) 11, 604 (1894).
(9).Jour.Phys.Chem. 12,,283,(1908).
(10).Ber. 35, 1256 (1902).
(11).Zeit. Phys. Chem. 28, 464 (1899).

Merck's highest quality pyridine was thoroughly dried over stick potassium hydroxide and then fractionated. The fraction passing over between 114° and 115° under a barometric pressure of 740 mm. was used in the experimentation.

The silver bromide was made from Merck's C.P. potassium bromide by precipitating from solution with a slight excess of silver nitrate. After thorough washing the precipitate was dried at 150° for several hours before and after grinding. The product had a pure yellow color and was rapidly attacked by sunlight.

The silver iodide was made in the same way from Merck C.P. potassium iodide. This was purified by means of washing with ammonia to remove any possible silver chloride present according to the method used by Ladenburg.(10)

The silver salt preparations as well as the solubility determinations were made in a faintly illuminated dark room.

The determinations of the solubility were made in the apparatus used by Meyerhoffer and Saunders(11), consisting of a hard glass tube fitted with a spiral stirrer and immersed in a constant temperature bath.

A water bath was used for temperatures 0° to 75°- above room temperature a gas thermo-regulator and below a metallic worm circulating ice water was used to keep the temperature constant. A paraffin bath was found good from 75° to 110°. Freezing mixtures of ice and salt were used from 0° to -20°. Below this temperature solid carbon dioxide

and ether were used.

A toluene thermometer graduated to degrees and permitting estimations to a tenth of a degree was used to read temperatures below zero degrees. Thermometers reading to tenths of a degree and carefully compared with the standards were used above 0°.

The temperature intervals between successive solubility determinations varied. In the neighborhood of transition points more determinations were made. The mixture of the salt and pyridine were stirred for about an hour at constant temperature. Where possible equilibrium was approached from the higher solubility to insure saturation. To test for this condition analysis was made of samples taken about an half hour apart.

A weighed portion of the solution was taken for a analysis. This was removed by means of a pipette the tip of which was capped with muslin. It was aimed to have the pipette at about the same temperature as the solution from which the sample was taken. The silver bromide and iodide were determined gravimetrically as such by the usual methods. The pyridine solution of the salt was diluted with water then a slight excess of nitric acid and a trace of silver nitrate solution added, After heating to incipient boiling the precipitate was collected on a Gooch crucible, washed and dried to a constant weight.at 150°

The results given in the following tables with the exception of those below 0° are the mean of two closely agreeing determinations. Below 0° this was not the case due to the difficulty in maintaining a constant temperature for a considerable period.

Following is the table of experimental results obtained in the system silver bromide and pyridine:-

Equilibrium between saturated solution and solid

$2AgBr.3C_5H_5N$

Temperature	AgBr Grams per 100 grams of pyridine.
-20.0 ° C.	3.59
-14.7	4.38
- 6.0	4.52
0.0	4.91
13.2	5.69
16.8	5.85
23.7	6.54
23.9	6.74
27.7	7.32
29.9	7.75
33.4	8.57
35.7	9.12

Transition point.

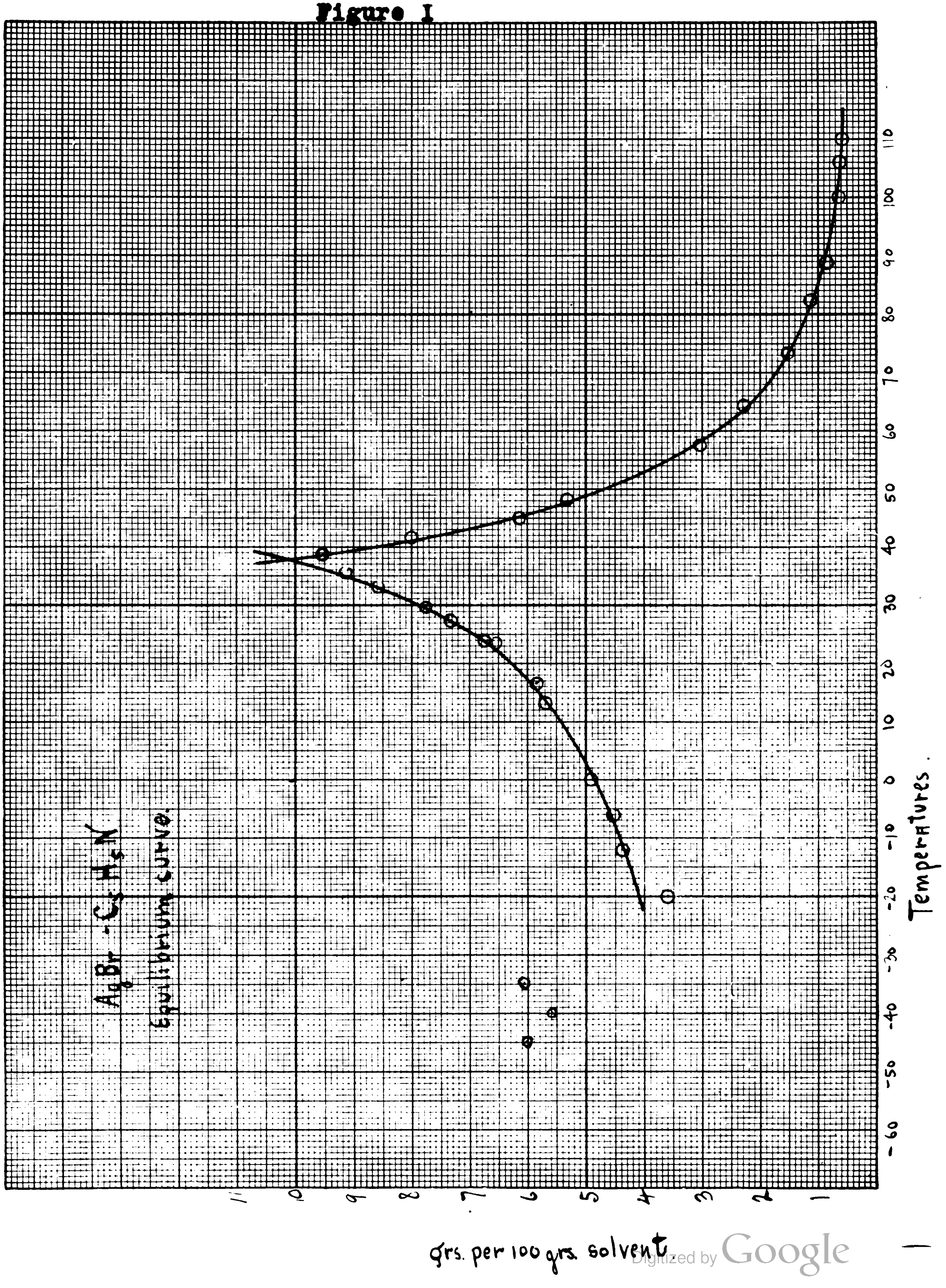
Equilibrium between saturated solution and solid AgBr.

38.8°C.	9.53
41.8	8.01
45.2	5.31
57.7	3.09
64.3	2.29
73.5	1?52
82.3	1.13
88.9	0.83
100.1	0.65
106.0	0.62
110.5	0.58

The above results are plotted in the accompanying figure (Fig. 1), the temperatures along the abscissa and the solubilities along the ordinate.

The determinations made below -20° and indicated on the diagram by the points in black circles, while permitting no definite conclusions regarding the form of the solubility curve there, yet show us that the solubility is higher at those lower temperatures. So it can be stated tentatively that in all probability other compounds of the bromide and pyridine exist at temperatures below -20°. That will be made the subject of further study.

Figure I


AgBr - C5H5N
Equilibrium curve.
Temperatures.
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
11
10
9
8
7
6
5
4
3
2
1
grs. per 100 grs. solvent.

From -20° up to about 37°.5 the solubility gradually increases. The solid in contact with the saturated solution between these temperatures has the composition $2AgBr.3C_5H_5N$. The crystals of this substance are white, silky and very thin lamellae which lose their pyridine very readily on exposure to the air. The crystals become yellww and lose their oder of pyridine. This compound shows partial fusion when the temperature is raised and the vapors of pyridine not allowed to escape. The mean of four analyses of this solid separating out at different temperatures between -20° and 37°.5 gives 60.1% silver bromide. The calculated percentage is 61.3%. The slightly low result is probably due to the difficulty in entirely removing the mother liquor.

From 37°.5 to 110° the solubility decreases, at first very rapidly and at the higher temperatures very slowly. The curve representing the change approaches in form a portion of a rectangular hyperbola. At these temperatures the solid phase present is the yellow crystalline silver bromide. In the neighborhood of 37°.5 there is a transition point at which the four phases vapor, saturated solution, $2AgBr.3C_5H_5N$ and AgBr are in equilibrium - a nonvariant system.

There is some indication of a break in the curve in the neighborhood of 20°. Analyses of the solid phase in contact with the saturated solution on both sides of this point gave closely agreeing figures, showing that possibly one or two of the points are not exactly on the true curve.

Following is the table of experimental results obtained in the system silver iodide and pyridine:-

Equilibrium between saturated solution and solid

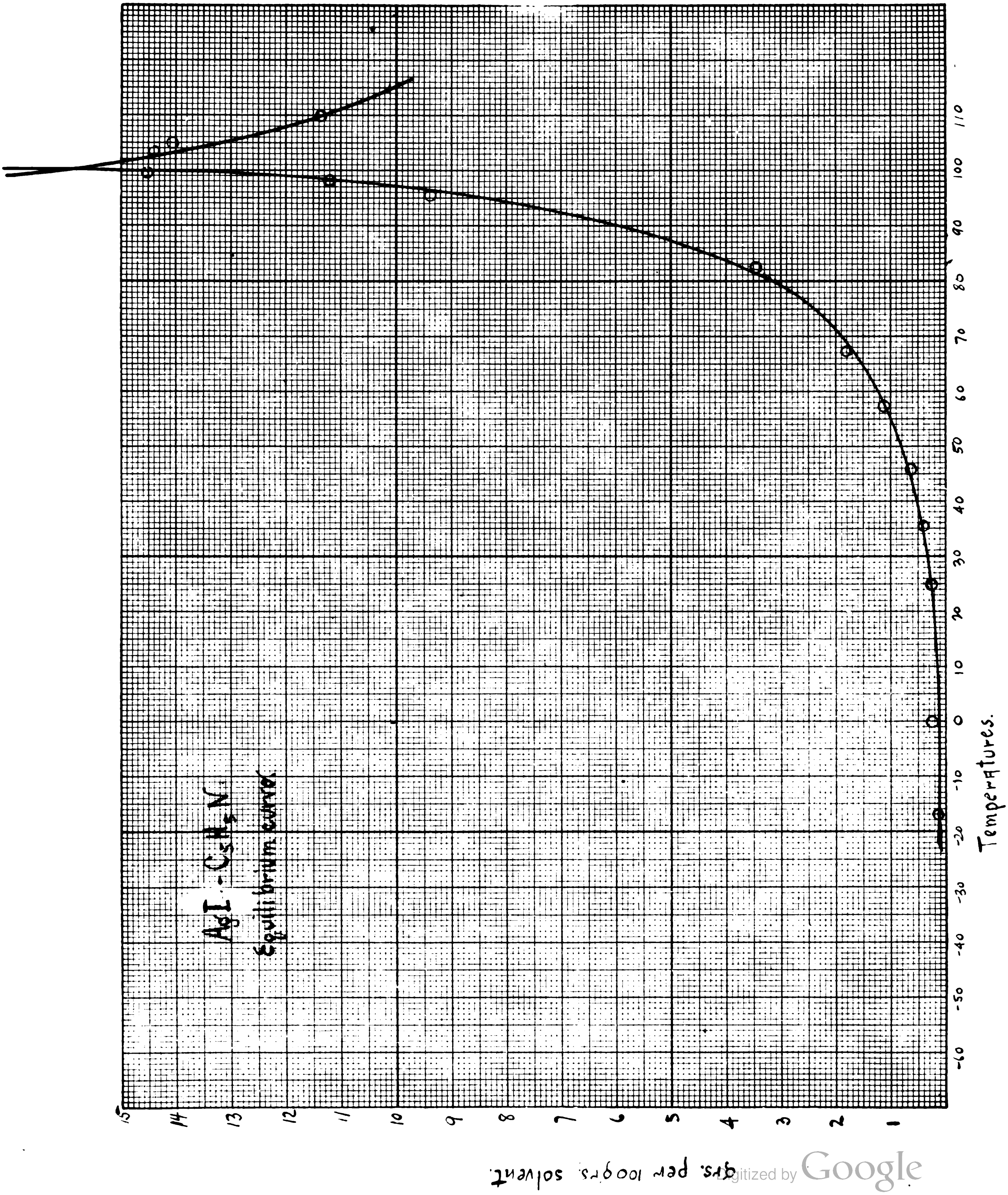
Temperature	$AgI.C_5H_5N$.	Grams AgI per 100 grams of pyridine.
-17.0° C.		0.12
0.0		0.23
25.0		0.25
35.5		0.40
45.9		0.63
57.5		1.11
67.5		1.81
82.5		3.47
95.2		9.40
98.2		11.20
99.7		14.52

Transition point.

Equilibrium between saturated solution and solid

	AgI	
103.5 °C		14.40
105.0		14.05
118.0		11.36

Figure II


AgI - C5H5N
Equilibrium curve
Temperatures.
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
grs. per 100 grs. solvent

The accompanying curve shows the above-given results in graphical form (Fig. II) plotted in same manner as in case of the preceeding curve.

From -17° to the neighborhood of 100° the solubility increases. Though no determinations were made below -17°, a qualitative examination showed that there was no marked increase in the solubility on going as low as -45°. The solubility increases very slowly at first, then very rapidly. During the temperature interval 80° to 100° it increases fourfold. The curve has the general appearance of a portion of a rectangular hyperbola, the asymptote going in the opposite direction, in reference to the temperature, as compared with the curve representing equilibrium of silver bromide with saturated solution. The solid phase in contact with the solution at these temperatures is $AgI.C_5H_5N$. The crystals of this compound are striated prismatic needles, white and silky in appearance. They lose their pyridine on exposure to the air but much more slowly than the bromide addition product described. It also shows the phenonemon of partial fusion. Analysis gives the percentage silver iodide as 74.0%. The calculated value is 74.8%.

At about 100° the solubility begins to rapidly decrease indicating a transition point. Here the four phases vapor, saturated solution, $AgI.C_5H_5N$, and silver iodide are in equilibrium. The analyses of the solid phase in contact with the solution above 100°, while not entirely satisfactory, point to

its being silver iodide. The other facts leading to this conclusion are the yellow color of the solid in contact with the boiling solution and that on removing and drying this the microscope shows a yellow nuclear crystal surrounded by the white addition product, which had separated from the mother liquor clinging to the crystals when they were cooled.

Summary and Discussion.

Above -20° there is one crystalline compound of pyridine and silver bromide, $2AgBr.3C_5H_5N$ hitherto unknown. There was no indication of the compound described by Varet (2). It appears as small lamellar, silky looking crystals losing their pyridine very rapidly under ordinary conditions of temperature and pressure. The equilibrium curve in the system silver bromide is given from about -20° to the boiling point of solvent.

There is one crystalline addition product of pyridine and silver iodide, $AgI.C_5H_5N$, stable above -20°. It appears as striated prismatic needles of a white color in contact with the saturated solution up to 100°. It loses its pyridine much slower than the bromide compound described above. The equilibrium curve in the system AgI and pyridine is established from about -20° to the boiling point ofthe solvent.

When the complete data in regard to the silver bromide are obtained it will be very interesting to compare the pyridine and the ammonia addition products of the three silver halides. A comparison of the curves (cf. ref 1) show many points of similiarity. In each case the solubility increases rapidly on

approaching from lower temperatures the transition point where the solid halide and the addition product are in equilibrium with the vapor and saturated solution constituting a quadruple point, then again falls off rapidly. The solubility curves of the solid halides insofar as they exist show the same general trend, the solubility decreasing with rise in temperature. The solubility increases in the order silver chloride, silver bromide and silver iodide which is also the order, in regard to temperature, of the transition points where the solid halide is present, respectively AgCl ; -1°; AgBr : 37°.5 ; AgI : 100°. It can be said that at a given temperature the specific chemical attraction of the pyridine for the silver halides increases in the above given order. In the case of ammonia the order is reversed apparently. This reversal is a very interesting fact.

Accepted,
July 31, 1908.
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